

METAL-ALCOHOLATE INITIATORS : SOURCE OF ANSWERS AND QUESTIONS IN RING-OPENING POLYMERIZATION OF HETEROCYCLIC MONOMERS

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In agreement with a former proposal by E. Vandenberg (1), polynuclear structures are a key feature for the design of catalysts able to polymerize substituted oxiranes into very high molecular weight polyethers. In an exploratory approach based on these premises and aimed at the synthesis of well characterized and versatile species of that type, we have shown indeed (2) that soluble μ -oxo-bimetallic trinuclear alkoxides having the general formula $[(RO)_xM^1-O-M^2-O-M^1(OR)_x]_n$ rank among the best known initiators for oxiranes polymerization, yielding products having molecular weights in the 10^6 range and displaying in some cases an amazing degree of stereoregularity despite the perfect solubility of the initiator and the polymer.

These compounds, particularly those where $M^1=Al$ and $M^2=Zn$, have proven to be very interesting models, allowing a better understanding of several determinant phenomena in ring opening polymerization, as well as in other areas of chemistry (3). It is the purpose of this paper to summarize the current status of the field, and to indicate its potential developments.

I. The polymerization of oxiranes

- The catalyst : although most compounds having the composition indicated above initiate oxiranes polymerization, their activity as well as the properties (i.e. M.W. and stereoregularity) of the resulting polymers depend critically on their structural characteristics : these include not only the composition, but also the size (degree of association of these coordinatively aggregated compounds) and the shape (coordination number and geometry around the metals).

The metal $(n-BuO)_4Al_2O_2Zn$ compound, with a mean degree of association $\bar{n}=6$ in non polar solvents is particularly efficient : the half-polymerization time of methyloxirane in heptane at $50^\circ C$ amounts to 5 minutes ! (with $[MO]=1M$, and $[Zn]=10^{-2}M$), and a M.W. between 1 and 2 millions is currently obtained. Furthermore, the direct relationship between the structure and the properties of this initiator has been confirmed by using oxo-alkoxides synthesized from two independent routes (2,4). These features, together with the stability of the catalyst, make of it one of the best candidates for a possible industrial production of high M.W. polyether rubbers.

- The initial polymerization period, extending up to a few percent conversion, is a typical autoacceleration period, during which the mean M.W. of the product increases and broadens significantly. More or less rapidly (depending on the structure) after that initial rearrangement, one enters an apparent steady-state situation, obeying simple kinetics and during which the mean molecular weight do not change very much anymore.

- The propagation is a coordinative process (as indicated from competition experiments with different solvents and comonomers), and proceeds on 3 different types of active centers (4,5) :

a) non-selective ones, producing oligomers by random opening of the oxirane ring (as indicated by NMR analysis and use of optically active monomer); however, these oligomers displaying an open-chain structure $H-[O-C_2H_4]_x-OR$ (after hydrolysis of the catalyst), exhibit particular lengths depending on the conditions and sometimes multimodal distributions, which are believed to reflect somehow the size and distribution of aggregates.

b) non-selective ones, but producing high M.W. atactic polymers, and stereoselective ones yielding isotactic high M.W. polyether. The degree of isotacticity, which can vary from 5 to 80 % depending on the conditions and structural parameters, relates clearly to the size and shape of the catalytic aggregate as indicated by experiments with $(RO)_4Al_2O_2CO^{II}$ compounds having different degrees of association and coordination geometries. It seems accordingly probable that these different but simultaneous pathways, take place through the same insertion propagation scheme yielding open-chain products of different lengths and stereoregularities, depending on the steric environment of the particular center involved, the relative amount and activity of each one being a sensitive function of the aggregate structure (the oligomer content can be reduced to 3 % of the total product).

- Correlation with the aggregate structure (6)

A detailed investigation by 1H , ^{13}C and ^{27}Al NMR spectroscopy has revealed a number of interesting characteristics of these coordination aggregates, which must have a globular type of structure (low and integer association numbers from cryoscopic measurements). The spectra indicate of course the presence of bridged and non-bridged OR groups, and of Al atoms with at least two different coordination environments. The most striking conclusion however is the unexpected rigidity of these structures as shown by the absorptions corresponding to the α and β carbons of the OR groups. Moreover, by using t-butyl oxirane which does not polymerize significantly at room temperature, one can observe the proportion of free and coordinated monomer (again a function of the aggregate structure) : here again, different types of coordination sites appear to be present.

Obviously, these observations might be correlated at least in part to the results reported above in terms of products distribution. They certainly illustrate the structural complexity of these systems, and support the general idea of a "topochemical control" of such polymerizations in solution, a borderline case between homogeneous and heterogeneous catalysis.

II. The activation of other substrates

- Lactones : the fast and perfectly living polymerization of lactones by complex aluminum alkoxides has now been well documented (7), where it is possible to control the catalyst efficiency by the nature of its ligands and the degree of association. This behaviour has opened the way to new block copolymerization methods : two of them are worthwhile to be mentioned here, although many other ones are to be expected :

a) the synthesis of caprolactone block copolymers with styrene or dienes (8), extremely useful as emulsifiers for the stabilization of different polymer blends (9);

b) the preparation of lactide block copolymers with other lactones, potentially interesting as biodegradable implants (10).

- Cumulenes : interestingly, μ -oxo-bimetallic alkoxides are also active towards heterocumulenes. Two important examples involve :

a) isocyanates, which are able to polymerize (11) to very high M.W. (10^6) polyamides-1, $-(N-CO)_n-$. Again

the resulting product, formed by insertion into the Al-OR bonds, contains an oligomer (cyclic trimer, isocyanurate, being the sole product above a T_c of ca. $70^\circ C$), and a bimodal high polymer (main product at low temperature and conversion).

b) carbon dioxide, which inserts slowly into all of the Al-OR bonds to produce the corresponding mixed carbonate. Under pressure (3B) and in the presence of methyloxirane, one obtains a copolymer containing ca. 25 % of carbonate units (12).

In conclusion, complex metal alkoxides and particularly those of aluminum, are very active and significant model compounds which can be tailored to better understand and control a variety of interesting reactions. In particular, they represent a rather unique example of surface-like behaviour in solution, and are certainly prone to broad extensions in different areas of chemistry (12,13). Other important questions, i.e. the understanding and control of termination reactions, certainly deserve further detailed study.

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